

# KEY PROPERTIES FOR THE OPTIMIZATION OF REFRACTORY CASTABLE DRYING

M. M. Akiyoshi, F. A. Cardoso, M. D. M. Innocentini and V. C. Pandolfelli, Department of Materials Engineering, Federal University of São Carlos 13565-905, S. Carlos, SP, Brazil, vicpando@power.ufscar.br

Drying is one of the most complex steps in refractory castable processing due to the considerable risk of damage or explosive spalling during the first heat-up. To provide a basis to optimize the drying step of refractory castables, this work correlates the mechanical strength and permeability with the mass loss rate and surface temperature profiles of high-alumina, ultra-low cement castables cured at different temperatures.

## 1. INTRODUCTION

The increasing demand for better and cheaper pre-cast refractory products has motivated the search for safer and shorter drying schedules in the refractory industry. However, drying is still a crucial step in castable processing, because improper heating schedules may lead to mechanical damage or even explosions when the tensile stress generated by pressurized vapor inside the refractory exceeds the material's mechanical strength.

Low curing temperatures of less than 20°C [1-8], followed by fast heating rates, have been identified as one of the most important factors to promote spalling. More comprehensive analyses have revealed that the curing temperature and its time affect permeability and mechanical strength, both associated with the likelihood of spalling [2, 3]. This work therefore aims to correlate the permeability and mechanical strength with the mass loss rate and surface temperature profiles of high-alumina, ultra-low cement castables cured at 10°C and 50°C, in order to provide the basis for a better understanding of this important step in the production of refractory castables.

## 2. EXPERIMENTAL PROCEDURE

The castables tested here consisted of high-alumina, ultra-low cement (2 wt%), containing 4.50 wt% of water (dry basis). The particle size distribution was adjusted to a theoretical curve, based on Andreasen's packing model with a coefficient of distribution of  $q=0.21$  (maximum aggregate size: 4.5 mm). Alcoa S.A. supplied all the raw materials, and further details of the composition are given elsewhere [3]. Castable samples having a 7.5 cm diameter and 2.5 cm thickness were prepared for the permeability tests, while those for the mechanical strength and drying tests were cast in the shape of 4 cm x 4 cm cylinders. The samples subjected to permeability and mechanical strength evaluations were pre-dried in silica gel at the curing temperature [7]. To evaluate the surface temperature, a thin K-type thermocouple (0.2 mm diameter) was inserted near the surface (1 mm depth) to record the sample's actual heating profile. The castables were cured at 10°C or 50°C (relative humidity of ~ 100%) for 48 h in a climatic chamber (Vötsch). Considering the same length of time [7], low curing temperatures provide a smaller degree of hydration than higher temperatures. Therefore, the castable samples were cured up to 16 days, allowing the ones cured at 10°C and those cured at 50°C to be exposed to a similar degree of hydration.

Mechanical strength was evaluated through a splitting test [9], at a loading rate of 42 N/s to keep the stress rate within a range of 690-1380 kPa/min. The splitting tensile strength was calculated by:

$$\sigma_f = \frac{2 \cdot P}{\pi \cdot h \cdot d} \quad (\text{MPa}) \quad (1)$$

where  $P$  (N) is the maximum load, and  $d$  (mm) and  $h$  (mm) are the samples' diameter and height, respectively.

Air permeability at room temperature was evaluated based on Forchheimer's equation [10] for compressible fluids and adjusting the  $k_1$  (Darcian) and  $k_2$  (non-Darcian) constants:

$$\frac{P_i^2 - P_o^2}{2 P_o L} = \frac{\mu}{k_1} v_s + \frac{\rho}{k_2} v_s^2 \quad (2)$$

where  $P_i$  (Pa) and  $P_o$  (Pa) are, respectively, the absolute air pressures at the entrance and exit of the sample,  $v_s$  (m/s) is the fluid velocity,  $L$  (m) is the sample's thickness,  $\mu$  (Pa·s) is the air viscosity and  $\rho$  (kg/m<sup>3</sup>) is the air density, evaluated for  $P_o = 690$  mmHg ( $92 \cdot 10^3$  Pa) and  $T = 25^\circ\text{C}$ .

Dewatering tests were performed in a thermogravimetric apparatus [11] consisting of a digital scale ( $400 \pm 0.001$  g) coupled to a furnace (maximum working temperature: 1000°C). The tendency for explosive spalling was evaluated at a heating rate of 20°C/min, while the drying profiles were performed at 10°C/min.

Mass loss during drying was assessed through the parameters  $W$  and  $W_d$ , defined as:

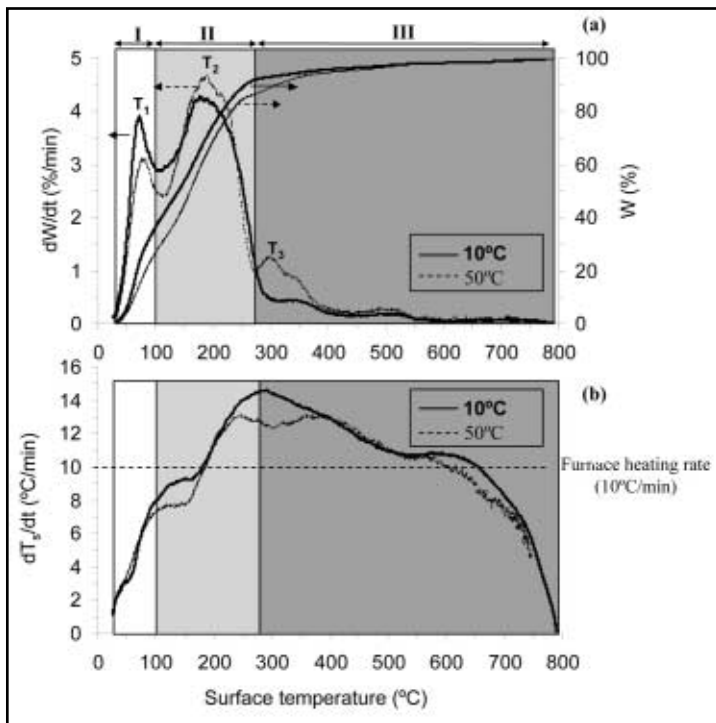
$$W = 100 \times \left( \frac{M_o - M}{M_o - M_f} \right) \quad (\%) \quad (3)$$

$$W_d = 100 \times \left( \frac{M_o - M}{M_f} \right) \quad (\%) \quad (4)$$

where  $M$  is the instantaneous mass recorded at time  $t_i$  during the heating stage,  $M_o$  is the initial mass and  $M_f$  is the final (dry) mass of the tested sample. The variable  $W$  evaluates the cumulative fraction of water expelled during the heat-up per total amount of water initially present in the body ( $W$  varied from zero to 100% during the test), while  $W_d$  relates the water loss to the dry weight of the body (in the range of 4.5% in the composition studied).

The mass loss and surface heating rates were then evaluated using equations (5) and (6), respectively.

$$\left( \frac{dW}{dt} \right)_i = \frac{d}{dt} \left( \frac{M_o - M}{M_o - M_f} \right) \quad (\%/min) \quad (5)$$



**Figure 1. (a) Mass loss (W) and mass loss rate (dW/dt); (b) surface heating rate (dT<sub>s</sub>/dt) for castables cured at 10°C or 50°C for two days. (Furnace heating rate: 10°C/min). Where: I – mainly evaporation, II – mostly ebullition and III – decomposition of hydrates.**

$$\left(\frac{dT_s}{dt}\right)_i = \left(\frac{T_{si+1} - T_{si-1}}{t_{i+1} - t_{i-1}}\right) \text{ (°C/min)} \quad (6)$$

In equation (6), T<sub>s</sub> is the surface temperature and t is the time.

### 3. RESULTS AND DISCUSSION

The castables cured at 10°C and 50°C are identified here as castable-10 and castable-50, respectively. Table 1 lists the explosion temperature at a 20°C/min heating rate, the splitting tensile strength (σ<sub>f</sub>) and the permeability constants (k<sub>1</sub> and k<sub>2</sub>) for the castables studied. As expected, the curing temperature and time affected the castable permeability and mechanical strength.

All the castables cured at 10°C (regardless of the curing time) exploded when tested at 20°C/min, while castable-50 did not undergo spalling. During two days of curing, castable-10 displayed lower permeability (k<sub>1</sub>=2.4•10<sup>-16</sup> m<sup>2</sup> and k<sub>2</sub>=176•10<sup>-16</sup> m) and lower mechanical strength (σ<sub>f</sub>=1.3 MPa) than did castable-50 (k<sub>1</sub>=3•10<sup>-16</sup> m<sup>2</sup>, k<sub>2</sub>=311•10<sup>-16</sup> m and σ<sub>f</sub>=2.0 MPa). These dif-

ferences confirmed the greater tendency for explosion of castables cured at low temperatures.

According to the literature [8-10], low curing temperatures induce the formation of low density hydrates such as CaO•Al<sub>2</sub>O<sub>3</sub>•10H<sub>2</sub>O (CAH<sub>10</sub>, ρ=1.72 g/cm<sup>3</sup>) and alumina gel, providing stronger and less permeable structures. On the other hand, at higher curing temperatures, denser hydrates such as 2CaO•Al<sub>2</sub>O<sub>3</sub>•8H<sub>2</sub>O (C<sub>2</sub>AH<sub>8</sub>, ρ=1.95 g/cm<sup>3</sup>), 3CaO•Al<sub>2</sub>O<sub>3</sub>•6H<sub>2</sub>O (C<sub>3</sub>AH<sub>6</sub>, ρ=2.52 g/cm<sup>3</sup>) and Al(OH)<sub>3</sub> (AH<sub>3</sub>, ρ=2.42 g/cm<sup>3</sup>) are formed and more permeable, weaker castables are generated.

The curing temperature affects the cement hydration kinetics [3,8], which is the main factor responsible for mechanical strength before firing. Although curing at low temperatures favors the formation of stronger structures, the lower mechanical strength after curing at 10°C for two days may be associated with the slower hydration rate of the cement at low temperatures. The greater strength attained in castable-10 after 16 days of curing reinforces this assumption. Due to its faster hydration kinetics, the hydration of castable-50 was almost complete after two days, while the mechanical strength of castable-10 increased continuously as the curing time progressed [3].

Despite its slower hydration rate, the permeability constants k<sub>1</sub> and k<sub>2</sub> were smaller for castable-10 due to the low density phases formed. The permeability continued to decrease as the curing time progressed because the amount of these phases increased as the hydration proceeded.

Comparing castable-10 cured for different lengths of time, one finds that, after 16 days, although its permeability was lower, its superior mechanical strength allowed the explosion temperature to increase from 426°C to 440°C. However, analyzing castable-10 and castable-50 cured for 16 days, the former's explosive spalling when heated at 20°C/min can be ascribed to its lower permeability, even though it displayed greater mechanical strength.

Correlations between mechanical strength, permeability and explosive tendency can be assessed by analyzing the mass loss and surface temperature profiles.

The drying steps of pre-fired, moistened, refractory castables subjected to a constant heating rate can be divided into three stages [11] that are associated, respectively, to the evaporation and the ebullition of free water, and the dehydration of chemically bonded water due to cement and reactive alumina hydration. The same association was used here to analyze the unfired castables cured at 10°C and 50°C. However, because unfired samples were used, the evaporation and ebullition profiles may show some overlapping contribution of the cement hydrate phases (CAH<sub>10</sub> and C<sub>2</sub>AH<sub>8</sub>) that decompose below 200°C.

**Table 1. Castable's curing temperature and time, explosion temperature (20°C/min heating rate), dry splitting tensile strength (σ<sub>f</sub>) and permeability constants (k<sub>1</sub> and k<sub>2</sub>).**

Curing time (days)	Curing Temperature (°C)	Explosion Temperature	σ <sub>f</sub> (MPa)	k <sub>1</sub> (10 <sup>-16</sup> m <sup>2</sup> )	k <sub>2</sub> (10 <sup>-16</sup> m)
2	10	426±3	1.3±0.1	2.4±0.1	176±17
	50	no explosion	2.0±0.3	3±1	311±023
16	10	440±7	2.9±0.4	1.0±0.1	19±1
	50	no explosion	2.0±0.2	2.2±0.1	189±23

**Table 2. Total amount of water (dry-basis), peak temperature ( $T_i$ ), and mass loss ( $W$ ) at each stage ( $i=1, 2$  or  $3$  for stages I, II or III, respectively) for castables cured at  $10^\circ\text{C}$  or  $50^\circ\text{C}$  for two days (results based on Figure 1a).**

Curing temperature ( $^\circ\text{C}$ )	$W_D$ (%)	$T_1$ ( $^\circ\text{C}$ )	$W_1$ (%)	$T_2$ ( $^\circ\text{C}$ )	$W_2$ (%)	$T_3$ ( $^\circ\text{C}$ )	$W_3$ (%)
10	4.49	75	38	189	55	363	7
50	4.36	82	32	180	54	304	14

Figure 1a presents the mass loss ( $W$ ) and the mass loss rate ( $dW/dt$ ), while Figure 1b shows the heating rate ( $dT_s/dt$ ) for castable samples cured for two days at  $10^\circ\text{C}$  and  $50^\circ\text{C}$ . The samples for these experiments were heated at  $10^\circ\text{C}/\text{min}$  (dashed line in Figure 1).

The actual mass loss rate is given by the balance between factors, which favors dewatering (evaporation, ebullition, and dehydration) and the receding of the drying front into the bulk of the castable. The amount of water lost ( $W$ ) in each drying stage (I, II or III) is illustrated in Figure 1a. Table 2 lists the results for each stage and curing condition.

Although the total amount of water used to prepare the castables was 4.50 wt%, castable-50 showed a lower  $W_d$  value (4.36 wt%) than castable-10 (4.49 wt%) because, even when curing is carried out in a moistened environment, higher temperatures favor the natural loss of water due to the reduction in water viscosity and the higher kinetic energy of its molecules.

In stage I (Figure 1a), the temperatures were lower than  $100^\circ\text{C}$  and evaporation was the main dewatering process. The lower water loss during the curing stage and the slower hydration kinetics favored a larger amount of free water in castable-10 than in castable-50. Thus, despite the lower permeability of castable-10, this composition lost a larger amount of water in stage I ( $W_1=38\%$ ) than did castable-50 ( $W_1=32\%$ ).

Also during stage I (Figure 1b), the heating rate of castables cured at  $10^\circ\text{C}$  and  $50^\circ\text{C}$  was similar because external factors, such as humidity and furnace heating rate, exerted a greater impact on evaporation than did permeability. In this stage, a fraction of the heat received by the sample was used to evaporate the water, slowing down the sample's heating rate when compared to the rate in the furnace ( $10^\circ\text{C}/\text{min}$ ). Because there was no pressurization of the structure in the first stage, even the weaker castable (cured at  $10^\circ\text{C}$  for two days) would not have been damaged had the drying taken place at temperatures below  $100^\circ\text{C}$ .

Water ebullition starts around  $100^\circ\text{C}$ , at which point the effects of the permeability levels become more relevant, because a larger amount of vapor can be entrapped within low permeability structures, raising the pressure inside the castable.

The permeability differences between castable-10 and castable-50 were evident above  $100^\circ\text{C}$  (stage II) from the discrepancies between their surface heating rates (Figure 1b). During ebullition, the vapor from the castable bulk reached the surface, preventing it from following the furnace heating rate. Because of its superior permeability, the vapor was released more rapidly from castable-50, resulting in a temporarily slower surface heating rate than that of castable-10.

During the ebullition stage, the vapor trapped inside the castable may become pressurized, and the less permeable the structure the greater the possibility of pressurization. Fracture or explosion will take place when the stress generated by the pressure surpasses the material's mechanical strength. Thus, the greater the mechanical strength, the higher the explosion temperature.

In the case of the samples tested here, after two days of curing, castable-50 presented a larger amount of hydrated phases than castable-10 [7], as indicated by the superior intensity of peak  $T_3$  in Figure 1a. This may represent an additional problem in castables with higher cement content because  $\text{C}_3\text{AH}_6$  and  $\text{AH}_3$  will decompose, reducing the mechanical strength and generating large amounts of vapor at higher temperatures.

In stage II, the amount of water loss in the castables was similar because part of the hydrates formed at  $50^\circ\text{C}$  decomposed below  $250^\circ\text{C}$ . Comparing the behaviors in stage III, castable-50 ( $W_3=14\%$ ) displayed a 7% higher weight loss than castable-10 ( $W_3=7\%$ ). This value (7%) is similar to the difference in the castables' water loss in the first stage.

The correlation of the mechanical strength and permeability with the mass loss and surface temperature profiles led to conclude that low permeability is the main cause for the tendency for explosive spalling of castables cured at low temperatures, since it favors the entrapment of vapor inside the structure, exposing the castable to higher pressures and higher real heating rates.


#### 4. CONCLUSIONS

In high-alumina, ultra-low cement castables, curing temperatures of  $10^\circ\text{C}$  and  $50^\circ\text{C}$  promoted significant differences in mechanical strength and permeability, whose effects were illustrated by the mass loss and surface heating rate profiles. The greater explosive tendency during the first heat-up for this class of castables cured at low temperatures ( $<20^\circ\text{C}$ ) can be associated with its low permeability and the presence of low density hydrates that decompose at temperatures close to  $100^\circ\text{C}$ . These hydrates increase the amount of water to be released within the ebullition range, and low permeability traps the vapor inside the refractory, generating pressurization and exposing the castable to higher pressures and higher real heating rates.

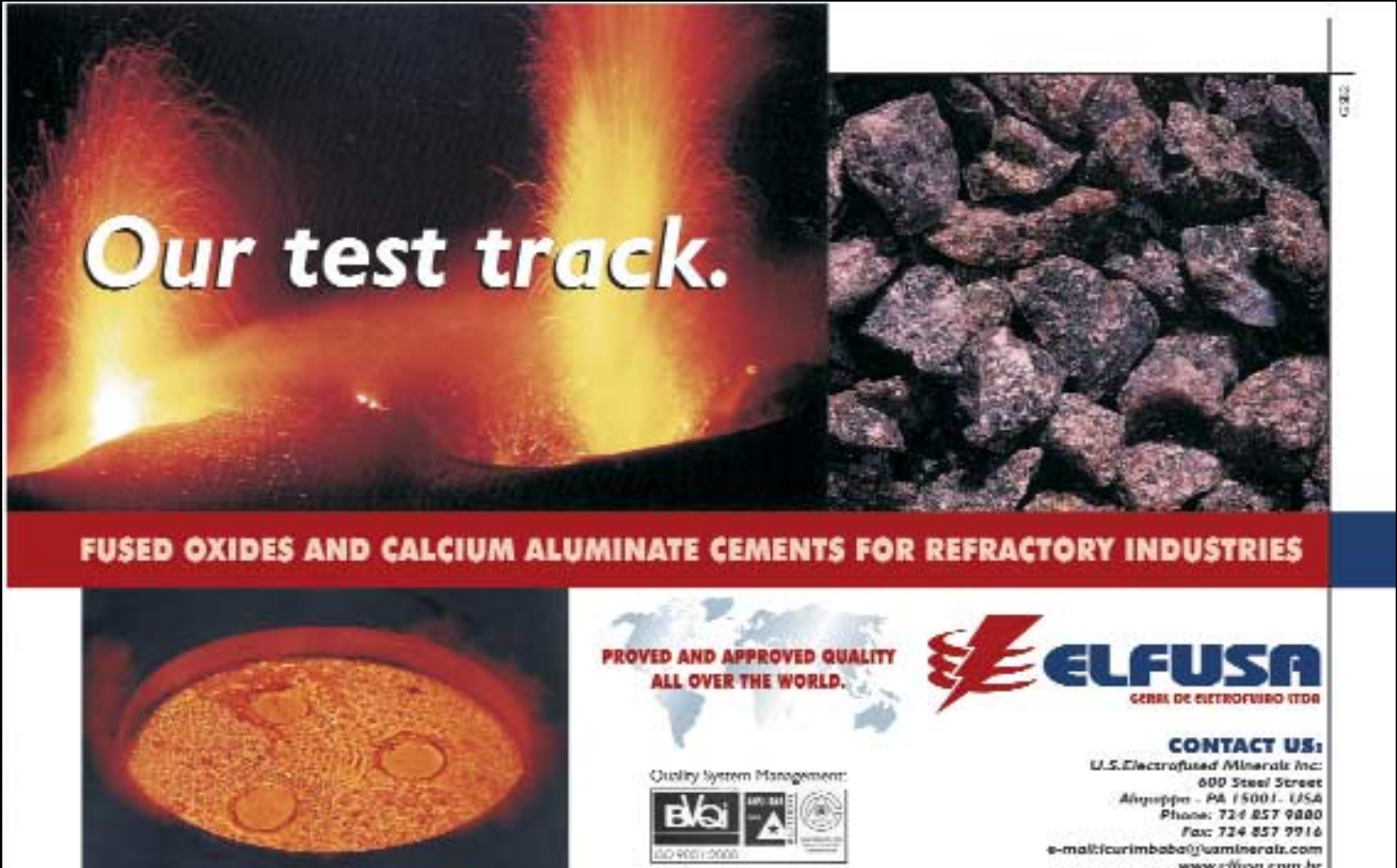
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